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Sea Water: Saturation with Apatites and Carbonates

Abstract. *Pacific Ocean water, on the average, appears to be slightly supersaturated at all temperatures with hydroxyapatite and carbonate fluorapatite. Water above 14°C is saturated with calcite, whereas water above 20°C is saturated with aragonite.*

Approximately 1200 analyses of Pacific Ocean water were examined to determine the average degree of saturation of sea water with hydroxyapatite, carbonate fluorapatite, calcite, and aragonite as a function of temperature (*1*). Calculations involving a large number of data in depth (approximately 0 to 3000 m) and area should show the general saturation level of the oceans with respect to the four minerals and should show temperature-saturation trends if present. The trends can be used to construct dynamic models for determining environments of formation for the minerals. Only analyses listing temperature, *p*H, alkalinity, total phosphorus, and salinity were used. All calculations and plotting were done by computer.

The degree of saturation of sea water with respect to hydroxyapatite, $\mathrm{Ca_{10}(PO_4)_6(OH)_2}$, may be determined by comparing pK'_{ap} with pK_{ap} (*2*):

$$pK'_{\mathrm{ap}} = 10\,p(\mathrm{Ca}^{2+}) + 6\,p(\mathrm{PO_4}^{3-}) + 2\,p(\mathrm{OH}^-) \qquad (1)$$

pK_{ap} is 111.69 (0°C), 112.00 (5°C), 113.19 (15°C), 113.99 (25°C), and 114.40 (30°C) (*3*).

The degree of saturation of sea water with respect to a carbonate fluorapatite,

$$\mathrm{Na_{0.29}Ca_{9.56}(PO_4)_{5.37}(SO_4)_{0.30}(CO_3)_{0.33}F_{2.04}},$$

may be determined by comparing pK'_{cfap} with pK_{cfap}:

$$\begin{aligned} pK'_{\mathrm{cfap}} = {} & 0.29\,p(\mathrm{Na}^+) + 9.56\,p(\mathrm{Ca}^{2+}) \\ & + 5.37\,p(\mathrm{PO_4}^{3-}) + 0.30\,p(\mathrm{SO_4}^{2-}) \\ & + 0.33\,p(\mathrm{CO_3}^{2-}) + 2.04\,p(\mathrm{F}^-) \qquad (2) \end{aligned}$$

pK_{cfap} is 103 at 5°C and 105 at 25°C as determined in this laboratory for this carbonate fluorapatite.

The saturation of sea water with aragonite and calcite may be determined by comparing pK'_{arag} with pK_{arag} and pK'_{calc} and pK_{calc}:

$$pK'_{\mathrm{arag}} = p(\mathrm{Ca}^{2+}) + p(\mathrm{CO_3}^{2-}) \qquad (3)$$

$$pK'_{\mathrm{calc}} = p(\mathrm{Ca}^{2+}) + p(\mathrm{CO_3}^{2-}) \qquad (4)$$

Activities of Ca^{2+}, $\mathrm{CO_3}^{2-}$, $\mathrm{PO_4}^{3-}$, Na^+, $\mathrm{SO_4}^{2-}$, F^-, and OH^- for substitution in Eqs. 1 through 4 are determined from the following relationships (*4*):

$$[\Sigma\mathrm{Ca}^{2+}] = [\mathrm{Ca}^{2+}] + [\mathrm{CaSO_4}^0]$$

$$\begin{aligned} \text{Alkalinity} = {} & 2[\mathrm{CO_3}^{2-}] + 2[\mathrm{CaCO_3}^0] \\ & + 2[\mathrm{MgCO_3}^0] + 2[\mathrm{NaCO_3}^-] + [\mathrm{HCO_3}^-] \\ & + [\mathrm{CaHCO_3}^+] + [\mathrm{MgHCO_3}^+] + [\mathrm{NaHCO_3}^0] \end{aligned}$$

$$\begin{aligned} [\Sigma\mathrm{PO_4}^{3-}] = {} & [\mathrm{HPO_4}^{2-}] + [\mathrm{H_2PO_4}^-] \\ & + [\mathrm{NaHPO_4}^-] + [\mathrm{KHPO_4}^-] + [\mathrm{MgHPO_4}^0] \\ & + [\mathrm{CaHPO_4}^0] + [\mathrm{Ca_2{\cdot}HPO_4{\cdot}CO_3}^0] \\ & + [\mathrm{Ca_2{\cdot}PO_4{\cdot}CO_3}^-] \end{aligned}$$

$$[\Sigma\mathrm{Na}^+] = [\mathrm{Na}^+] + [\mathrm{NaSO_4}^-]$$

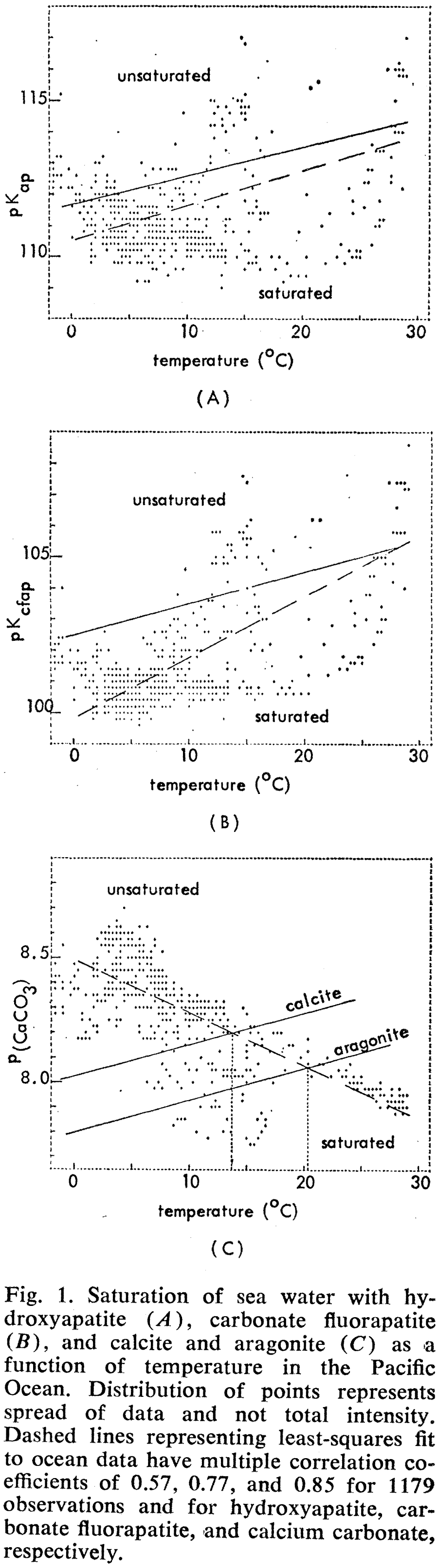
$$[\Sigma\mathrm{K}^+] = [\mathrm{K}^+] + [\mathrm{KSO_4}^-]$$

$$\begin{aligned} [\Sigma\mathrm{SO_4}^{2-}] = {} & [\mathrm{SO_4}^{2-}] + [\mathrm{MgSO_4}^0] + [\mathrm{CaSO_4}^0] \\ & + [\mathrm{NaSO_4}^-] + [\mathrm{KSO_4}^-] \end{aligned}$$

$$[\Sigma\mathrm{F}^-] = [\mathrm{F}^-] + [\mathrm{MgF}^+]$$

The values of pK' in Eqs. 1 through 4 were plotted by computer, and a least-squares curve of the form, $pK' = (a/t) + b$, was fitted to the data. The dashed line in Fig. 1 is the least-squares fit to data, whereas the solid line represents the solubility constant as a function of temperature.

Sea water on the average appears to be supersaturated with respect to hydroxyapatite and carbonate fluorapatite as is shown by comparing dashed and solid lines in Fig. 1, *A* and *B*. There is, however, only a 1 to 2 percent difference from equilibrium values for the values of pK'. Arrhenius (*5*) found, contrary to these conclusions, that apatite is being dissolved in deep ocean water environments. Some of



(A)

(B)

(C)

Fig. 1. Saturation of sea water with hydroxyapatite (*A*), carbonate fluorapatite (*B*), and calcite and aragonite (*C*) as a function of temperature in the Pacific Ocean. Distribution of points represents spread of data and not total intensity. Dashed lines representing least-squares fit to ocean data have multiple correlation coefficients of 0.57, 0.77, and 0.85 for 1179 observations and for hydroxyapatite, carbonate fluorapatite, and calcium carbonate, respectively.

the assumptions made in doing the calculations may not be valid, and the bias may result in apparent supersaturation results. The value of pK' for fluorapatite [$Ca_{10}(PO_4)_6F_2$, which is not shown] is 10^5 greater than the corresponding pK for all data; yet fluorapatite is not encountered in recent or ancient sediments. $Ca_2 \cdot HPO_4 \cdot CO_3^0$ and $Ca_2 \cdot PO_4 \cdot CO_3^-$ account for a great deal of the dissolved phosphate in sea water. The lack of consideration of these two ligands would increase pK' for the apatites by approximately 10^{10} (*6*). Since CO_2 appears in amounts varying up to 4 percent in CO_2-F-apatite (*7*), the stoichiometry and solubility constant used here are probably not representative of the total temperature range.

Sea water is saturated and unsaturated with respect to calcite and aragonite, as shown by the fields marked by the two solid lines in Fig. 1*C*. On the average, sea water 14°C or warmer appears to be saturated with calcite, and sea water 20°C or warmer is saturated with aragonite. These boundary temperatures probably represent minimum average temperature limits for obviously precipitating carbonate environments. It is interesting to note that the 20°C limit for aragonite corresponds to the minimum average surface water temperature associated with 30° north and south latitude limits of carbonate formation in the present oceans (*8*).

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Prehistoric Archeological Surveys and Excavations in Afghanistan: 1959–1960 and 1961–1963

Abstract. *Afghanistan has long been considered an important transmitter of culture in the historic periods. Buddhism, for example, reached the Far East from Gandhara (the classical name for southern Afghanistan and parts of northwestern West Pakistan). Recent research indicates that the foothills of northern Afghanistan may have been one of the early centers of incipient agriculture, transitional between the food gathering of the Paleolithic and the food production of the Neolithic. In addition, Upper and possibly Middle ("Mousterian") Paleolithic industries have been identified.*

In many archeological studies in the Near and Middle East since World War II, attempts have been made to locate and define the zones of the development of agriculture and the domestication of animals, the two important processes by which man learned to control his food supply (*1*). Earlier botanical studies indicated the possibility that the highlands of Afghanistan might also be an early center for the domestication of the wheat-barley complex of the Old World (*2*). Beginning in 1949, a series of expeditions to the Afghan-Pakistani area were organized for the purpose of investigating the prehistory of the region. Several monographs have been published on the findings of the first two (1949, 1950–51) expeditions (*3*).

In this report I describe tentatively some of the results of work at Darra Dadil-Darra Chakhmakh, Qala Shaharak, and Ghar-i-Mar (Snake Cave).

I conducted an extensive survey of northern Afghanistan during November and December 1959, and recorded over 100 caves and 150 mounds of archeological interest. Surface collections on many of the mounds yielded types of pottery which might be prehistoric (*4*). Also, the periglacial terraces of the Darra Dadil and Darra Chakhmakh valley (south of Mazar-i-Sharif near the town of Aq Kupruk, 36°05′N, 66°51′E), now completely dried-up stream beds, yielded several hundred flint cores and flake tools (primarily scraper types) of possible "Mousterian" affinities (*5*).

In October 1961, Klaus Fischer and I dug a test pit in a mound near Qala Shaharak (34°07′N, 54°25′E) in the western Hindu Kush mountains about 260 km east of Herat (34°20′N, 62°12′E). We collected painted pottery with possible prehistoric affinities from 30 separate mounds in the valley of Shaharak. No historic glazed pottery appeared in the test pit, but the ages of the lower and upper levels, estimated by radiocarbon dating, indicated that pottery samples were 1085 ± 120 years (Hv 206) and 720 ± 110 years (Hv 205) old, respectively (*6*). The range, therefore, extends from about A.D. 900 to 1200, possibly a remarkable case of cultural lag, which indicates that much more work should be done on the later historic painted wares of the Middle East (*7*). However, the possibility that the samples used for radiocarbon dating were contaminated cannot be completely ignored.

The second excavations took place during July and August 1962, at the rock shelter of Ghar-i-Mar (Snake Cave), located on a high terrace of the Balkh River in the limestone hills of the Hindu Kush mountains about 100 km south of Mazar-i-Sharif near the aforementioned town of Aq Kupruk. In a stepped trench, 24 m long by 2 m wide, I reached a depth of about 10.5 m (Figs. 1 and 2). The tentative sequence can be described briefly as follows.

Modern nomads still use the rock shelter for sheep and goat pens while moving through the area, and the upper levels consist mainly of sheep and goat dung.

The Early Islamic levels contain green and blue glazed sherds similar